NAT'L INST. OF STAND & TECH R.I.C.
A11104 245466

DEPARTMENT OF COMMERCE

BULLETIN
OF THE
BUREAU OF STANDARDS

VOLUME 9

1913

41

DATE DUE

10-10-92	859988		

Demco, Inc. 38-293

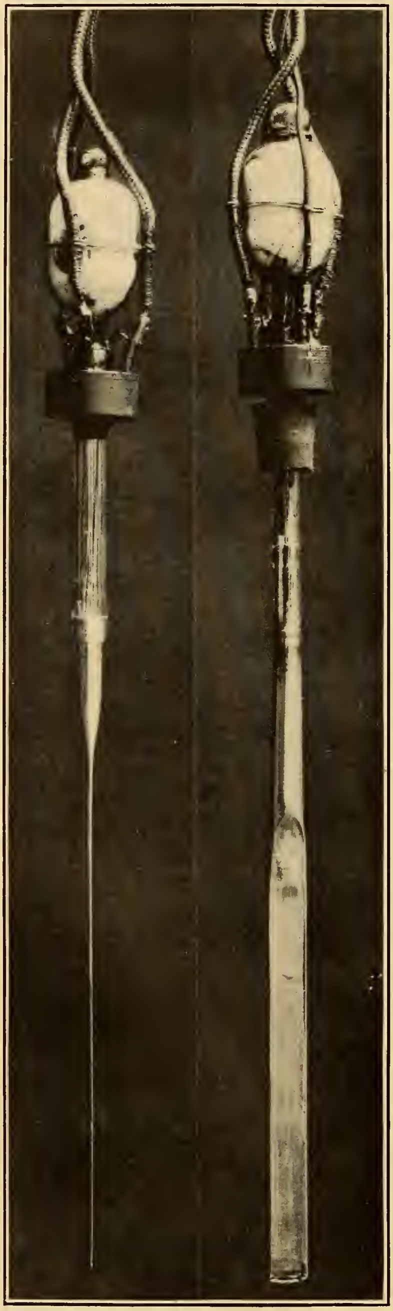

Fig. 1.—*New form of calorimetric resistance thermometers.*

NEW CALORIMETRIC RESISTANCE THERMOMETERS

By H. C. Dickinson and E. F. Mueller

Since the publication of the paper "Calorimetric Resistance Thermometers and the Transition Temperature of Sodium Sulphate"[1] improvements made in the type of resistance thermometer there described have changed it from a special laboratory instrument into one of extensive application for precision measurements of temperature in the interval −180° to +180°, or, with slight modifications, up to 500°[2]. Since these instruments have now been put on the market and a considerable number are in use, a description of the newer form may be of interest.

This paper is intended merely as a general description and not as a set of working directions. Information as to methods of construction and necessary precautions will be furnished to anyone desiring to make thermometers of this type.

The thermometers described in the earlier paper were somewhat limited in their applicability because of the presence of solder in the sheath, of hard rubber at the upper end of the sheath, and of a wax joint between the metal and the hard-rubber head. The wire used was 0.02 mm in diameter, which limited the sensibility by reducing the allowable measuring current, thus rendering necessary the use of very sensitive galvanometers.

The type of thermometer now in use is the result of a gradual development in the course of which a number of thermometers have been constructed. Two of the new thermometers are shown in Fig. 1 and details of construction in Fig. 2. The changes made have led to a greater ease of construction, robustness, reliability, and general utility.

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[1] This Bulletin, 3, p. 640, Reprint No. 68.

[2] Up to this time these instruments have actually been used only between the limits of −180° and +150°.

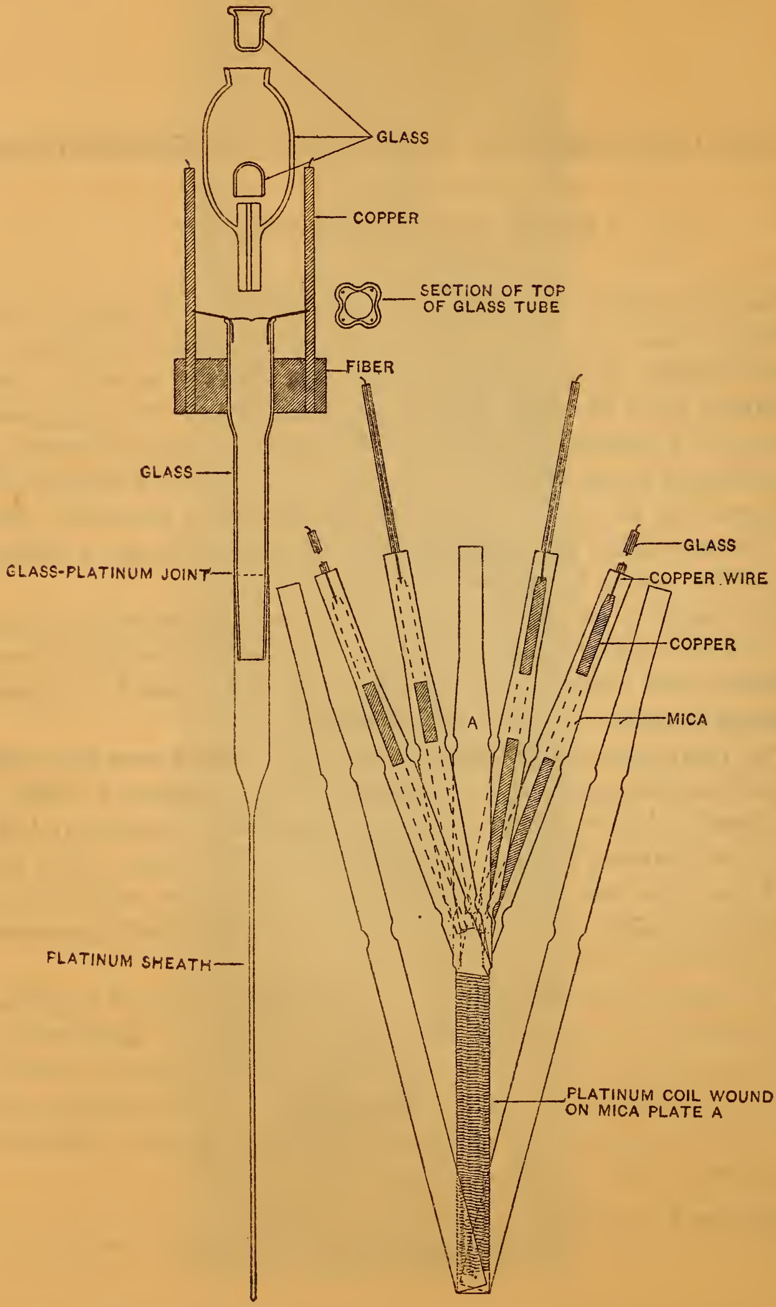

Fig. 2.—*Diagrammatic sketch of parts of thermometer, separated to show construction.*

Coil.—The coil is of the purest Heraeus platinum wire 0.1 mm in diameter, a length of about 2.2 meters being wound in a flat bifilar coil about 8 cm long and 7 mm broad, on one end of a mica strip, which is about 18 cm long, and 0.2 mm. thick.

The turns of wire are held in place by notches in the sides of the mica strip and are spaced about 14 turns to the centimeter. The coil is insulated from the surrounding sheath by strips of mica somewhat wider and thinner than that on which the coil is wound. Before winding, the wire is annealed by heating to a high temperature, 1000° to 1200° C by passing an electric current through it. After winding and attaching the leads, i. e., after the coil is so far completed as not to require further handling, it is carefully washed in distilled water to remove all traces of hygroscopic salts and is then heated to a bright red by means of an electric current to drive off all volatile matter, and to reanneal the wire.

Leads.—Three forms of connection are adapted to use respectively with (a) a shunted bridge only; (b) a shunted bridge or a slide-wire bridge; (c) a shunted bridge, a Kelvin bridge, a differential galvanometer, or a potentiometer. The connections are made as shown in Fig. 3. In all three types the effect of lead resistance is eliminated.

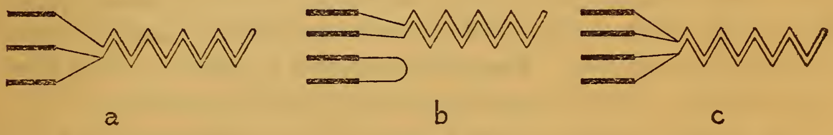

Fig. 3

The leads for any of these forms are made of thin strips of No. 36 B. & S. gage (0.13 mm) copper 2 to 3 mm wide; but in a single thermometer all are made alike. In the forms (a) and (c) the copper lead is separated from the branch point by from 15 to 20 mm of the 0.1-mm platinum wire. In the form (b) the compensating loop is closed by a piece of this wire 3 or 4 cm long. All platinum joints are made by fusing with an arc, using a pure graphite electrode, while the copper platinum joints are made either by welding or with silver, using borax as a flux. The flat copper strips extend to just beyond the mica strips, where they are silver-soldered to No. 20 copper wires, which are threaded through glass tubes. If suitable rolls are available, it is preferable to roll down the wires at the ends to take the place of the copper strips.

Sheath.—The sheaths are made of thin drawn silver or (preferably) platinum tubes 7 mm in diameter, 15 to 18 cm long, and of about 0.12 mm wall thickness for the platinum and up to 0.2 mm for the silver. These tubes are partially flattened, as shown in Fig. 1, and after the coil is inserted are closed at the ends by fusing with an arc, and pressed down onto the coil.

Heads.—The heads are made entirely of glass and consist of four pieces, as shown in Fig. 2—the stem, drying capsule, and two small caps. The stems are usually attached to the metal cases by platinizing the glass, which is just large enough to slip into the metal tube, and then soldering the glass and metal together with ordinary soft solder. As this solder melts at about 190° C, thermometers to be used above this temperature have the case made of platinum, which is fused directly to the glass. This method requires a rather large joint between the glass and platinum. The glass must be of special composition (such as Jena 397^{III}) and the work carefully done to avoid breaking at this point.

The upper part of this tube is shaped to provide grooves for the lead wires, which are brought out between the tube and the stem of the drying capsule. The drying capsule is sealed in with Khotinski cement, the wires passing out through this cement.

The drying capsule is about half filled with asbestos wool, the small inside glass cap serving to prevent loose particles from dropping into the tube below. The rest of the capsule is filled with phosphorus pentoxide. When the small upper cap is cemented on, the thermometer is kept warm to prevent the internal pressure becoming larger than one atmosphere when the thermometer is subsequently used at the higher temperatures.

Outside leads.—The coil leads are soldered to pins or small copper tubes held in a fiber collar which is cemented to the glass stem. To these pins or tubes the flexible leads of No. 18 or No. 20 silk-covered lamp cord are attached. These leads are as nearly as possible alike, both as to length and total resistance, and preferably not more than 2 or 3 m long. The battery leads in forms (a) and (c) may be of No. 22 wire. These wires are so protected at the soldered joints as to prevent sharp bending. This may be accomplished by threading the wire through the copper tubes and making the soldered joint at the lower end.

Essential Features.—It is worth while to emphasize some of the points to which attention had to be given to make thermometers of this type successful. Some of these are essential to the success of any type of resistance thermometer and have been duly emphasized in many other publications. The more important are:

1. Securing and maintaining a *high insulation resistance* by taking care when making up the coils to secure absolute cleanliness and freedom from foreign matter and then sealing a drying agent inside the thermometer.

2. Mounting in such a way as to avoid subjecting the resistance wire to strains.

3. Providing close contact between the wire, insulating material, and sheath (the total thickness is less than 1 mm), reducing the lag, and thereby allowing the use of a relatively large measuring current.

4. Using the compensating leads to eliminate not only the effect of variable resistance of the thermometer leads due to varying temperatures, but also the effect of thermal conduction in these leads by having a loop of the same wire which is used for the coil attached to the compensating leads.

5. *Eliminating thermoelectric troubles* due to copper-platinum junctions by having all such junctions down in the sheath close together, where they will all be immersed in the bath the temperature of which is to be measured.

All of these features, with the possible exception of the drying agent, are essential to this type of thermometer.

Constants of the Thermometers.—The thermometers made, up to the present time, have been constructed to have a resistance such that the change between 0° and 100° C is very nearly 10 ohms, which requires a resistance of about 25.6 ohms at a temperature of 0° C. Computation of temperatures, and particularly of temperature differences, is very much facilitated by this means, since nearly all computations can be made with a 10-inch slide rule.

If the thermometer is to be used solely for calorimetric work, a resistance of 25.3 ohms at 0° C is convenient, giving about 0.1 ohm per degree at 20°.

The wire used in these thermometers being of the purest platinum obtainable, the fundamental coefficient is 0.00391 as against 0.00336 for the wire used in the older type. The value of δ (in the Callendar formula) is for these thermometers about 1.47 when computed from observations at 0°, 50°, and 100° or at 0°, 32°.384, and 100° as against 1.55 for the older thermometers.

Measuring Current.—The current generally used with these thermometers is 5 to 6 milliamperes. This causes a rise of temperature of the wire above that of a water bath in which the thermometer is immersed, of the order of 0°.002, varying somewhat in individual thermometers. This amount of heating is entirely permissible when measurements are to be made to 0°.0001, since the current may change by over 2 per cent without producing a change of 0°.0001. In fact, the measuring current is limited, not by the amount of the heating but by the fact that the bridge is unbalanced with the current off, so that closing the battery circuit causes a throw of the galvanometer. It is the desirability of limiting the heating so that equilibrium, within the limit of reading, shall be established in a time not much longer than the period of the galvanometer swing, that fixes the convenient limit to the measuring current.

Performance.—The behavior of these thermometers has been very satisfactory, although some have proven a little more constant than others. The best of them have shown variations of less than 0°.001, in melting ice from time to time, during two years or more; what proportion of this observed change is attributable to the thermometer and what to the resistance coils of the bridge and the standard of reference or to the actual changes in the temperature of the ice bath is uncertain. Such variations do not necessarily produce any such error in the measurement of temperature changes. In fact, there is nothing to indicate that these thermometers are unreliable for such measurements even to the extent of 0°.0001. The thermometers mentioned were of the 3-lead (Fig. 3, *a*) type, so that the variations referred to include variations in the stranded leads. Inasmuch as this has been considered a serious source of error,[3] it is well to call particular attention to this point. With care in handling leads the variations have never exceeded 0.0001 ohm.

Defects.—The variations in the resistance of the stranded leads may become serious if they are carelessly handled so as to break one or more strands. This will manifest itself by erratic changes in the apparent resistance when the thermometer is at a constant temperature. Other causes of variation such as strains in the wire will usually be detected and should be eliminated during the original calibration.

The presence of moisture in the thermometer, due to a leak or to exhaustion of the drying material, may occur. The resulting phenomena are very characteristic and easily recognized. If the bridge, with the thermometer in circuit and galvanometer circuit closed and a key in the battery circuit, is balanced by adjusting resistance with the battery key closed, then on opening the battery circuit there will be a large deflection of the galvanometer, which gradually diminishes and on closing it again, another large deflection in the opposite direction. The latter slowly diminishes if the circuit is kept closed. This phenomenon is readily distinguished from that due to the use of an excessive measuring current, by the absence of the galvanometer deflection in the latter case, when the battery circuit is opened.

The presence of moisture also reduces the insulation resistance between the coil and sheath. This insulation resistance is easily tested and should exceed 200 megohms.

Difference Formula.—The ordinary Callendar equations are very convenient for most computations, but for computation of temperature differences the calculation may be made much more simple by the use of a single factor.

The Callendar equations are

$$pt = \frac{R_t - R_o}{R_{100} - R_o} 100, \text{ or since } R_{100} - R_o = R_o\,(100c)$$

$$pt = \frac{R_t - R_o}{R_o c} \qquad (1)$$

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[3] F. E. Smith: Phil. Mag. [VI], 24, p. 542; 1912.

and

$$t - pt = \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \tag{2}$$

These two equations are easily combined into a single one

$$R_t = R_0(1 + \alpha t + \beta t^2) \text{ where} \tag{3}$$

$$\alpha = c\left(1 + \frac{\delta}{100}\right) \text{ and } \beta = -\frac{c\delta}{100^2}$$

Suppose the difference of two temperatures t_1 and t_2 is to be computed from the corresponding values R_1 and R_2 we have,

$$\begin{aligned} R_2 &= R_o\ (1 + \alpha t_2 + \beta\, t_2^2) \\ R_1 &= R_o\ (1 + \alpha t_1 + \beta\, t_1^2) \\ R_2 - R_1 &= R_o\ [\alpha(t_2 - t_1) + \beta\ (t_2 - t_1)\ (t_2 + t_1)] \\ &= R_o\ (t_2 - t_1)\ (\alpha + 2\ \beta\ T) \end{aligned}$$

$$\text{Where } T = \frac{t_2 + t_1}{2} = \text{mean } t$$

$$\text{Then } t_2 - t_1 = \frac{1}{R_o(\alpha + 2\ \beta T)}(R_2 - R_1)$$

or

$$\Delta t = \frac{1}{R_o\ (\alpha + 2\beta\ T)}\Delta\ R \tag{4}$$

This is of the same form as the formula obtained by differentiation

$$\delta t = \frac{1}{R_o\ (\alpha + 2\ \beta t)}\ \delta R$$

and the condition that the formula hold for finite differences is that T be the mean of the two temperatures, t_1 and t_2, the difference of which is to be measured.

The formula may be rewritten in terms of the constants used in the Callendar formula

$$\Delta t = \frac{100}{(R_{100} - R_o)\left(1 + \frac{\delta}{100} - \frac{2\delta T}{100^2}\right)}\Delta\ R \tag{5}$$

From (5) a table of factors may be computed as follows: A series of values of $\overline{R}$, the mean of R_1 and R_2 is assumed, the corresponding values of T are then computed and substituted in the formula. This table is then used as an interpolation table to find Δt when R_1 and R_2 are given.

The computation for a thermometer which has the constants $R_o=25.3012$, $R_{100}-R_o=9.8902$, $\delta=1.47$ is given in the table below.

R	pt	T	$\frac{100}{R_{100}-R_o}$	$1+\frac{\delta}{100}-\frac{2\delta T}{100^2}$	Factor
26.8	15.154	14.97	10.1110	1.01030	10.0079
9	16.165	15.97	10.1110	01000	109
27.0	17.176	16.97	10.1110	00971	138
1	18.188	17.97	10.1110	941	168
2	19.199	18.97	10.1110	912	197
3	20.210	19.97	10.1110	882	226
4	21.221	20.98	10.1110	853	255
27.5	22.232	21.98	10.1110	823	285
6	23.243	22.98	10.1110	794	314
7	24.254	23.99	10.1110	765	343
8	25.265	24.99	10.1110	735	372

As the constants from which the table is derived warrant an accuracy of only 1 in 10 000, the factors in the last column would in practice be carried out only to the third decimal place.

When using such a thermometer, e. g., in a calorimetric measurement, all calculations, such as that for cooling correction, etc., are made in terms of resistance instead of temperature, and the final value R_2-R_1 for the change in resistance is multiplied by the appropriate factor corresponding to $\overline{R}=\frac{R_2+R_1}{2}$, to find t_2-t_1.

It appears that an error due to this method of calculation may be introduced, since the factor which should be used is that corresponding to $T=\frac{t_2+t_1}{2}$, while the one actually used is that corresponding to the t defined by $\overline{R}=R_o\ (1+\alpha t+\beta t^2)$. It is easily shown, however, that the error is insignificant. If we write $t_2-t_1=\tau$, then a simple calculation shows that

$$T-t=\frac{-\beta\tau^2}{4\{\alpha+\beta(T+t)\}}=\frac{-\beta\tau^2}{4(\alpha+2\beta T)}\text{ approximately.}$$

If $\tau=10^\circ$ and $T=0^\circ$, then from the above $T-t=0^\circ.0036$, the result depending only in a minor degree on T. From the table of factors it is seen that the factor changes by about 30 parts in 100 000 per degree, so that the error for a 10° rise amounts to about 1 in 1 000 000. Since the error increases as the square of the temperature difference, it follows that the table can be used for differences up to 30° before the error becomes as large as 1 in 100 000.

Summary.—An improved form of calorimetric resistance thermometer is described and some points of interest in connection with its use are given.

A difference formula for simplifying calorimetric computations is given and its applicability shown.

WASHINGTON, January 1, 1913.